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(12) **United States Patent**  
**Shekhter et al.**(10) **Patent No.:** **US 8,715,386 B2**  
(45) **Date of Patent:** **\*May 6, 2014**(54) **PROCESS FOR PREPARING METAL POWDERS HAVING LOW OXYGEN CONTENT, POWDERS SO-PRODUCED AND USES THEREOF**(75) Inventors: **Leonid N. Shekhter**, Ashland, MA (US); **Steven A. Miller**, Canton, MA (US); **Leah F. Haywiser**, Arlington, MA (US); **Rong-Chein R. Wu**, Chelmsford, MA (US)(73) Assignee: **H.C. Starck Inc.**, Newton, MA (US)

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None

See application file for complete search history.

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*Primary Examiner* — George Wyszomierski(74) *Attorney, Agent, or Firm* — Bingham McCutchen LLP(57) **ABSTRACT**

In various embodiments, low-oxygen metal powder is produced by heating a metal powder to a temperature at which an oxide of the metal powder becomes thermodynamically unstable and applying a pressure to volatilize the oxygen.

**54 Claims, No Drawings**

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**PROCESS FOR PREPARING METAL  
POWDERS HAVING LOW OXYGEN  
CONTENT, POWDERS SO-PRODUCED AND  
USES THEREOF**

RELATED APPLICATIONS

This application is a continuation of U.S. patent application Ser. No. 12/444,263, filed Oct. 5, 2009, now U.S. Pat. No. 8,226,741, which is a U.S. national stage application of International (PCT) Patent Application Serial No. PCT/US2007/080282, filed Oct. 3, 2007, which claims the benefit of U.S. patent application Ser. No. 11/542,055, filed Oct. 3, 2006 now abandoned. The entire disclosure of each of these applications is incorporated by reference herein.

BACKGROUND OF THE INVENTION

Passive oxide layers are inherent to all metal powders. In general, the presence of such oxides has an adverse effect on one or more of the properties of the products made from such powders.

For example, due to the high melting point of tantalum, its purification method yields a metal powder. When exposed to air, tantalum oxidizes and forms an oxide layer, which protects it from further oxidation. In order to make metal parts, this powder must be consolidated to solid form. Due to the inherent stability of this oxide layer, when pressed and sintered into a powder metallurgy form, the oxygen is conserved, yielding a lower quality product. Therefore the oxygen removal becomes a primary objective for tantalum refining.

The operation of oxygen removal is called deoxidation. There is quite a bit of art teaching various ways of removing oxygen. One way to avoid this oxygen is to electron beam melt the powder, vaporizing the oxygen, resulting in an ingot with only the ingot's passive layer of oxygen.

A second known method for removal of oxygen from tantalum is using another element to reduce Ta<sub>2</sub>O<sub>5</sub>. One element that can be used is carbon (see, e.g., U.S. Pat. No. 6,197,082). However, since excess carbon is used for reduction, tantalum carbides result as a contaminant. U.S. Pat. No. 4,537,641 suggests using magnesium, calcium, or aluminum as the reductant (see also U.S. Pat. Nos. 5,954,856 and 6,136,062). These metals can be then leached out of the tantalum with water and diluted mineral acid, U.S. Pat. Nos. 6,261,337, 5,580,516 and 5,242,481 suggest this method for use on low surface area powders, which are used in the manufacture of solid tantalum parts. The byproduct of this process is a layer of MgO on the surface of the tantalum powder. As such it is necessary to expose this powder to air and water during the leaching and drying processes, creating the passive oxide layer. Another potential contaminant, which may result during this process, is magnesium. Magnesium tantalates are stable enough to survive the pressing and sintering processes that yield solid tantalum parts.

European Patent 1,066,899 suggests purifying tantalum powder in thermal plasma. The process was carried out at atmospheric pressure, at the temperatures exceeding the melting point of tantalum in the presence of hydrogen. The resulting powder had spherical morphology and the oxygen concentration as low as 86 ppm.

A more recent development for the removal of oxygen from tantalum is the use of atomic hydrogen as described in U.S. patent application Ser. No. 11/085,876, filed on Mar. 22, 2005. This process requires significant hydrogen excess and is thermodynamically favorable in a relatively narrow tem-

perature range. Theoretically this process is capable of producing very low oxygen powder.

Other techniques for reducing the oxygen content of tantalum are described in U.S. Pat. No. 4,508,563 (contacting tantalum with an alkali metal halide), U.S. Pat. No. 4,722,756 (heating the tantalum under a hydrogen atmosphere in the presence of an oxygen-active metal), U.S. Pat. No. 4,964,906 (heating the tantalum under a hydrogen atmosphere in the presence of a tantalum getter metal having an initial oxygen content lower than the tantalum), U.S. Pat. No. 5,972,065 (plasma arc melting using a gas mixture of helium and hydrogen), and U.S. Pat. No. 5,993,513 (leaching a deoxidized valve metal in an acid leach solution).

Other techniques for reducing the oxygen content in other metals are also known. See, e.g., U.S. Pat. Nos. 6,171,363, 6,328,927, 6,521,173, 6,558,447 and 7,067,197.

Cold spray technology is the process by which materials are deposited as a solid onto a substrate without melting. During the cold spray process, the coating particles are typically heated by carrier gas to only a few hundred degrees Celsius, and are traveling at a supersonic velocity typically in the range of 500 to 1500 meters per second prior to impact with the substrate.

The ability to cold spray different materials is determined by their ductility, the measure of a material's ability to undergo appreciable plastic deformation. The more ductile the raw materials, the better the adhesion attained during the cold-spray process due to its ability to deform.

Different metals have different plastic properties, soft metals, with excellent ductility characteristics, therefore have been used in the cold spray technology, such as copper, iron, nickel, and cobalt as well as some composites and ceramics.

In the family of refractory metals, currently only tantalum and niobium are used, as they are the softest of the refractory metals. Other refractory metals such as molybdenum, hafnium, zirconium, and particularly tungsten are considered brittle, and therefore cannot plastically deform and adhere upon impact during cold spray.

Metals with body centered cubic (BCC) and hexagonal close-packed (HCP) structures exhibit what is called a ductile-to-brittle transition temperature (DBTT). This is defined as the transition from ductile to brittle behavior with a decrease in temperature. The refractory metals, which perform poorly when cold-sprayed, exhibit a higher DBTT. The DBTT, in metals, can be impacted by its purity. Oxygen and carbon are notoriously deleterious to the ductility. Due to their surface area and affinity for oxygen and carbon, these elements tend to be particularly prevalent impurities in metal powders. Since the cold-spray process requires metals powders as a raw material, it makes the use of high DBTT refractory metals prohibitive, with the exception of tantalum and niobium, which have lower DBTT.

DESCRIPTION OF THE INVENTION

The present invention is directed to the discovery that the oxygen content can be drastically reduced by creating conditions at which the refractory oxide species become thermodynamically unstable, and removed by volatilization. The main challenge was to find the thermodynamic parameters (temperature and total pressure) at which the oxide species became unstable and volatilize while the metal species will continue to stay in the condensed phase.

More particularly, the present invention is broadly directed to a process for the preparation of a metal powder having a purity of at least as high as the starting powder and having an oxygen content of 10 ppm or less comprising heating the

metal powder containing oxygen in the form of an oxide, with the total oxygen content being from 50 to 3000 ppm, in an inert atmosphere at a pressure of from 1 bar to  $10^{-7}$  to a temperature at which the oxide of the metal powder becomes thermodynamically unstable and removing the resulting oxygen via volatilization. The process has the additional advantage of significantly reducing and/or removing any metallic impurities having boiling points lower than that which the oxide of the metal powder becomes thermodynamically unstable.

The metal powder is preferably selected from the group consisting of tantalum, niobium, molybdenum, hafnium, zirconium, titanium, vanadium, rhenium and tungsten.

The inert atmosphere can be substantially any "inert" gas, such as argon, helium, neon, krypton or xenon.

When the metal powder is tantalum, such powder is heated in an inert gas atmosphere at a pressure of from 1 bar to  $10^{-7}$  bar and a temperature of from about 1700° C. to about 3800° C. The resultant unpassivated powder has a purity of at least as high as the starting powder, and preferably at least 99.9%, a surface area of from about 100 cm<sup>2</sup>/g to about 10,000 cm<sup>2</sup>/g, an oxygen content of 10 ppm or less, a hydrogen content of 1 ppm or less, a magnesium content of 1 ppm or less, an alkali metal content of 1 ppm or less, and a combined iron plus nickel plus chromium content of 1 ppm or less. As noted above, the process has the advantage of significantly reducing any metallic impurities (such as alkali metals, magnesium, iron, nickel and chromium) having boiling points lower than the temperature at which the tantalum oxide becomes thermodynamically unstable.

When the metal powder is niobium, such powder is heated in an inert gas atmosphere at a pressure of from  $10^{-3}$  bar to  $10^{-7}$  bar and a temperature of from about 1750° C. to about 3850° C. The resultant unpassivated powder has a purity of at least as high as the starting powder, a surface area of from about 100 cm<sup>2</sup>/g to about 10,000 cm<sup>2</sup>/g, an oxygen content of 10 ppm or less, a hydrogen content of 1 ppm or less, a magnesium content of 1 ppm or less, an alkali metal content of 1 ppm or less, and a combined iron plus nickel plus chromium content of 1 ppm or less.

When the metal powder is tungsten, such powder is heated in an inert gas atmosphere at a pressure of from 1 bar to  $10^{-7}$  bar and a temperature of from about 1200° C. to about 1800° C. The resultant unpassivated powder has a purity of at least as high as the starting powder, a surface area of from about 100 cm<sup>2</sup>/g to about 10,000 cm<sup>2</sup>/g, an oxygen content of 5 ppm or less, a carbon content of 5 ppm or less and a hydrogen content of 1 ppm or less.

When the metal powder is molybdenum, such powder is heated in an inert gas atmosphere at a pressure of from 1 bar to  $10^{-7}$  bar and a temperature of from about 1450° C. to about 2300° C. The resultant unpassivated powder has a purity of at least as high as the starting powder, a surface area of from about 100 cm<sup>2</sup>/g to about 10,000 cm<sup>2</sup>/g, an oxygen content of 10 ppm or less and a hydrogen content of 1 ppm or less.

When the metal powder is titanium, such powder is heated in an inert gas atmosphere at a pressure of from  $10^{-3}$  bar to  $10^{-7}$  bar and a temperature of from about 1800° C. to about 2500° C. The resultant unpassivated powder has a purity of at least as high as the starting powder, a surface area of from about 100 cm<sup>2</sup>/g to about 10,000 cm<sup>2</sup>/g, an oxygen content of 10 ppm or less and a hydrogen content of 1 ppm or less.

When the metal powder is zirconium, such powder is heated in an inert gas atmosphere at a pressure of from  $10^{-3}$  bar to  $10^{-7}$  bar and a temperature of from about 2300° C. to about 2900° C. The resultant unpassivated powder has a purity of at least as high as the starting powder, a surface area

of from about 100 cm<sup>2</sup>/g to about 10,000 cm<sup>2</sup>/g, an oxygen content of 10 ppm or less and a hydrogen content of 1 ppm or less.

When the metal powder is hafnium, such powder is heated in an inert gas atmosphere at a pressure of from  $10^{-3}$  bar to  $10^{-7}$  bar and a temperature of from about 2400° C. to about 3200° C. The resultant unpassivated powder has a purity of at least as high as the starting powder, a surface area of from about 100 cm<sup>2</sup>/g to about 10,000 cm<sup>2</sup>/g, an oxygen content of 10 ppm or less and a hydrogen content of 1 ppm or less.

From the kinetic standpoint, it is generally preferable to run the process at the temperatures above the melting point of the particular metal as both chemical and diffusion processes proceed at a higher rate in the molten state. The temperature of the system should not be too high in order to minimize the evaporation of the particular metal.

The range of temperatures described above can usually be reached using the gas plasma process. The temperature in the plasma flame is not constant; due to the particle size distribution, it may not be possible to heat all particles to the set temperature. Since the residence time in the plasma flame is extremely short, the particles inherently will be at different temperatures. Therefore, there is a potential to underheat the coarse particles (not enough volatilization) and overheat the fine particles (excessive volatilization, not only of the metal oxide but also the metal itself). It is, however, not the only means of reaching the desired temperature range. For example, the induction melting can be also used.

The requirements of temperature and pressure can be met by using vacuum plasma technique, or other equipment such as electric-resistant furnace, rotary kiln, induction furnace, e-beam furnace in high vacuum and the like. The equipment that is preferable is one that is capable of vacuum and allows flexible residence time.

The process of the invention allows for the production of a metal powder with very low oxygen content typical of the consolidated solid metal. This was made, possible due to the application of the process requiring no reducing agent. The prior art used either magnesium or hydrogen for the reduction of oxygen and therefore, the product (powder) had to be passivated (exposed to air) prior to its further usage.

Processing metal powders under the conditions described has the additional advantage of significantly reducing and/or removing any metallic impurities having boiling points lower than that which the oxide of the metal powder becomes thermodynamically unstable (e.g., depending upon the starting metal powder, such impurities as iron, nickel, chromium, sodium, boron, phosphorous, nitrogen and hydrogen may be significantly reduced). In the case of tantalum, the nitrogen content will be reduced to 20 ppm or less and the phosphorous content will be reduced to 10 ppm or less. Another reaction that will occur under these conditions would be the removal of carbon due to the reaction of the carbide with the oxide. This is particularly important in the case of tungsten, even small amounts of oxygen and carbon can make the tungsten brittle. It is critical to reduce carbon (to a level of 5 ppm or less) and oxygen (to a level of 5 ppm or less) from tungsten to a level at which the tungsten becomes ductile and therefore useable in the cold spray process.

The powder particles produced via the process of the invention have virtually the same low oxygen content regardless of their size. Furthermore, the obtained powder has this low oxygen content regardless of its surface area. Depending on the total pressure, the powder may or may not have to be melted. The powder may be used as a raw material for the ensuing operations without removal of either fine or coarse fraction. Powder can be produced in different types of fur-

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naces including but not limited to plasma, induction, or any resistance furnace capable of working under vacuum.

The process of the invention is a relatively low cost process since it does not require any reducing agent, is a one step process, does not call for the product passivation, does not require screening out powder fractions, and could be run continuously. Moreover, due to the low oxygen and other impurities content, the obtained powder will be of superior grade quality.

Due to the extremely high reactivity of the powder in air, its transfer and further treatment or usage has to be done in the inert atmosphere until the powder is fully consolidated. If the final product is to be used in a cold spray process, it is important that the material not be exposed to any oxygen containing atmosphere before it is sprayed. This can be achieved by either storage under vacuum or other inert gas. For the same reason, the use of inert gas during the cold spray process is necessary.

The result of the present invention is the drastic reduction of the oxygen and carbon contents, for example, that would increase the ductility of the previously unusable refractory metals, and make them potentially usable. This would potentially expand the usage of previously high DBTT metals.

The products of the present invention and blends thereof can be used as raw material for the cold spray process for sealing gaps in refractory metal cladding, for producing sputtering targets, for the rejuvenation of used sputtering targets, for the coating of different geometries in electronics, chemical industrial processes, and other market segments and for X-ray anode substrates. The low content of oxygen and other impurities will dramatically improve the consolidation process.

In addition, the products can be used for pressing and sintering of different components, tools and parts. For example, the powders and their blends can be used in both CIP and HIP processes. Low content of oxygen and other impurities will lead to an extremely high sintering activity of the powders. This will allow for the production of sputtering targets with the content of oxygen and other impurities comparable to that of the standard roiling process.

The products of the invention could also be used in a cold spray process to produce near net-shape parts.

The drastic decrease of oxygen and other impurities could potentially allow for the production of parts via powder metallurgy processes which will be comparable to those produced via standard melting/rolling techniques.

Although illustrated and described herein with reference to certain specific embodiments, the present invention is not intended to be limited to the details described. Various modifications may be made within the scope and range of equivalents of the claims that follow without departing from the spirit of the invention.

The invention claimed is:

1. A method of producing low-oxygen metal powder, the method comprising:

heating a metal powder comprising 50 ppm to 3000 ppm oxygen to a temperature at which an oxide of the metal powder becomes thermodynamically unstable, the metal powder being selected from the group consisting of tantalum, niobium, molybdenum, hafnium, zirconium, titanium, vanadium, rhenium, and tungsten; and thereduring, applying a pressure within the range of  $10^{-7}$  bar to  $10^{-3}$  bar, thereby volatilizing the oxygen and forming a low-oxygen metal powder, wherein the low-oxygen metal powder has an oxygen content of 10 ppm or less.

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2. The method of claim 1, wherein the metal powder is heated in a hydrogen-free atmosphere.

3. The method of claim 1, wherein the metal powder is heated in an atmosphere comprising at least one of argon, helium, neon, krypton, or xenon.

4. The method of claim 1, wherein the metal powder is heated in an atmosphere substantially free of magnesium.

5. The method of claim 1, wherein the low-oxygen metal powder has a hydrogen content of 1 ppm or less, a magnesium content of 1 ppm or less, and an alkali metal content of 1 ppm or less.

6. The method of claim 1, wherein heating the metal powder comprises gas-plasma heating, induction heating, or resistance heating.

7. The method of claim 1, wherein a surface area of the low-oxygen metal powder ranges from approximately 100  $\text{cm}^2/\text{g}$  to approximately 10,000  $\text{cm}^2/\text{g}$ .

8. The method of claim 1, further comprising, after forming the low-oxygen metal powder, spray depositing the low-oxygen metal powder.

9. The method of claim 8, wherein the low-oxygen metal powder is spray deposited after formation without passivating the low-oxygen metal powder therebetween.

10. The method of claim 8, wherein spray depositing comprises cold spray.

11. The method of claim 1, wherein the metal powder is tungsten and the oxygen content of the low-oxygen metal powder is 5 ppm or less.

12. A method of producing low-oxygen metal powder, the method comprising:

heating a metal powder comprising 50 ppm to 3000 ppm oxygen in a hydrogen-free atmosphere to a temperature at which an oxide of the metal powder becomes thermodynamically unstable; and

applying a pressure within the range of  $10^{-7}$  bar to 1 bar, thereby volatilizing the oxygen and forming a low-oxygen metal powder,

wherein the low-oxygen metal powder has an oxygen content of 10 ppm or less.

13. The method of claim 12, wherein the metal powder is selected from the group consisting of tantalum, niobium, molybdenum, hafnium, zirconium, titanium, vanadium, rhenium, and tungsten.

14. The method of claim 12, wherein the hydrogen-free atmosphere comprises at least one of argon, helium, neon, krypton, or xenon.

15. The method of claim 12, wherein the hydrogen-free atmosphere is substantially free of magnesium.

16. The method of claim 12, wherein the low-oxygen metal powder has a hydrogen content of 1 ppm or less, a magnesium content of 1 ppm or less, and an alkali metal content of 1 ppm or less.

17. The method of claim 12, wherein heating the metal powder comprises gas-plasma heating, induction heating, or resistance heating.

18. The method of claim 12, wherein a surface area of the low-oxygen metal powder ranges from approximately 100  $\text{cm}^2/\text{g}$  to approximately 10,000  $\text{cm}^2/\text{g}$ .

19. The method of claim 12, further comprising, after forming the low-oxygen metal powder, spray depositing the low-oxygen metal powder.

20. The method of claim 19, wherein the low-oxygen metal powder is spray deposited after formation without passivating the low-oxygen metal powder therebetween.

21. The method of claim 19, wherein spray depositing comprises cold spray.

22. The method of claim 12, wherein the metal powder is tungsten and the oxygen content of the low-oxygen metal powder is 5 ppm or less.

23. A method of producing low-oxygen metal powder, the method comprising:

heating a metal powder comprising 50 ppm to 3000 ppm oxygen to a temperature at which an oxide of the metal powder becomes thermodynamically unstable; and applying a pressure within the range of  $10^{-7}$  bar to 1 bar, thereby volatilizing the oxygen and forming a low-oxygen metal powder,

wherein the low-oxygen metal powder has an oxygen content of 10 ppm or less and a hydrogen content of 1 ppm or less.

24. The method of claim 23, wherein the metal powder is selected from the group consisting of tantalum, niobium, molybdenum, hafnium, zirconium, titanium, vanadium, rhenium, and tungsten.

25. The method of claim 23, wherein the metal powder is heated in a hydrogen-free atmosphere.

26. The method of claim 23, wherein the metal powder is heated in an atmosphere comprising at least one of argon, helium, neon, krypton, or xenon.

27. The method of claim 23, wherein the metal powder is heated in an atmosphere substantially free of magnesium.

28. The method of claim 23, wherein the low-oxygen metal powder has a magnesium content of 1 ppm or less and an alkali metal content of 1 ppm or less.

29. The method of claim 23, wherein heating the metal powder comprises gas-plasma heating, induction heating, or resistance heating.

30. The method of claim 23, wherein a surface area of the low-oxygen metal powder ranges from approximately 100  $\text{cm}^2/\text{g}$  to approximately 10,000  $\text{cm}^2/\text{g}$ .

31. The method of claim 23, wherein the pressure is within the range of  $10^{-7}$  bar to  $10^{-3}$  bar.

32. The method of claim 23, further comprising, after forming the low-oxygen metal powder, spray depositing the low-oxygen metal powder.

33. The method of claim 32, wherein the low-oxygen metal powder is spray deposited after formation without passivating the low-oxygen metal powder therebetween.

34. The method of claim 32, wherein spray depositing comprises cold spray.

35. The method of claim 23, wherein the metal powder is tungsten and the oxygen content of the low-oxygen metal powder is 5 ppm or less.

36. A method of producing low-oxygen metal powder, the method comprising:

heating a metal powder comprising 50 ppm to 3000 ppm oxygen in a hydrogen-free atmosphere to a temperature at which an oxide of the metal powder becomes thermodynamically unstable; and

thereduring, applying a pressure within the range of  $10^{-7}$  bar to  $10^{-3}$  bar, thereby volatilizing the oxygen and forming a low-oxygen metal powder,

wherein the low-oxygen metal powder has an oxygen content of 10 ppm or less.

37. The method of claim 36, wherein the metal powder is heated in an atmosphere comprising at least one of argon, helium, neon, krypton, or xenon.

38. The method of claim 36, wherein the metal powder is heated in an atmosphere substantially free of magnesium.

39. The method of claim 36, wherein the low-oxygen metal powder has a hydrogen content of 1 ppm or less, a magnesium content of 1 ppm or less, and an alkali metal content of 1 ppm or less.

40. The method of claim 36, wherein heating the metal powder comprises gas-plasma heating, induction heating, or resistance heating.

41. The method of claim 36, wherein a surface area of the low-oxygen metal powder ranges from approximately 100  $\text{cm}^2/\text{g}$  to approximately 10,000  $\text{cm}^2/\text{g}$ .

42. The method of claim 36, further comprising, after forming the low-oxygen metal powder, spray depositing the low-oxygen metal powder.

43. The method of claim 42, wherein the low-oxygen metal powder is spray deposited after formation without passivating the low-oxygen metal powder therebetween.

44. The method of claim 42, wherein spray depositing comprises cold spray.

45. The method of claim 36, wherein the metal powder is tungsten and the oxygen content of the low-oxygen metal powder is 5 ppm or less.

46. A method of producing low-oxygen metal powder, the method comprising:

heating a metal powder comprising 50 ppm to 3000 ppm oxygen to a temperature at which an oxide of the metal powder becomes thermodynamically unstable; and thereduring, applying a pressure within the range of  $10^{-7}$  bar to  $10^{-3}$  bar, thereby volatilizing the oxygen and forming a low-oxygen metal powder,

wherein the low-oxygen metal powder has an oxygen content of 10 ppm or less, a hydrogen content of 1 ppm or less, a magnesium content of 1 ppm or less, and an alkali metal content of 1 ppm or less.

47. The method of claim 46, wherein the metal powder is heated in an atmosphere comprising at least one of argon, helium, neon, krypton, or xenon.

48. The method of claim 46, wherein the metal powder is heated in an atmosphere substantially free of magnesium.

49. The method of claim 46, wherein heating the metal powder comprises gas-plasma heating, induction heating, or resistance heating.

50. The method of claim 46, wherein a surface area of the low-oxygen metal powder ranges from approximately 100  $\text{cm}^2/\text{g}$  to approximately 10,000  $\text{cm}^2/\text{g}$ .

51. The method of claim 46, further comprising, after forming the low-oxygen metal powder, spray depositing the low-oxygen metal powder.

52. The method of claim 51, wherein the low-oxygen metal powder is spray deposited after formation without passivating the low-oxygen metal powder therebetween.

53. The method of claim 51, wherein spray depositing comprises cold spray.

54. The method of claim 46, wherein the metal powder is tungsten and the oxygen content of the low-oxygen metal powder is 5 ppm or less.